Trimethyl Phosphite Adsorbed on Silica: An NMR and Infrared Study

Ian D. Gay,*

*Department of Chemistry, Simon Fraser University, Burnaby, British Columbia,
Canada V5A 1S6*

A. J. McFarlan, and B. A. Morrow*

Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada, K1N 6N5 (Received: June 4, 1990)

Infrared spectroscopy and phosphorus-31 magic angle spinning nuclear magnetic resonance spectroscopy have been used to study the adsorption of trimethyl phosphite (TMP) on silica. At 23 °C TMP reacts rapidly with surface silanol groups to give $SiOCH_3$ as a chemisorbed product and liquid dimethyl phosphite (DMP). However, formation of DMP ceases when about half of the SiOH groups have been consumed because DMP strongly hydrogen bonds to the remaining silanols thereby inhibiting further reaction between TMP and SiOH. TMP also undergoes isomerization to dimethyl methylphosphonate (DMMP) which is catalyzed by SiOH. As the number of initial silanol groups is decreased (by using higher temperatures of vacuum activation) the quantity of DMP produced decreases whereas that of DMMP increases. A mechanism for formation of DMP and DMMP has been suggested. At 100 °C isomerization does not occur, all SiOH groups are consumed, and the major product is $DMP/SiOCH_3$ accompanied by a small quantity of a chemisorbed phosphorus-containing species having the proposed structure $(SiO)_2P-H(=O)$. The latter is stable up to 400 °C. If TMP is heated with silica from 100 to 400 °C, in addition to $SiOCH_3$, the major new chemisorbed product of the reaction which can be identified by IR and NMR is $(SiO)_2P-Me(=O)$ (Me = CH_3). The advantages of a combined IR-NMR approach are discussed.

Introduction

The interaction of phosphorus compounds with oxides has been of considerable recent interest on two accounts. One is related to the enhanced acidity of phosphate-impregnated oxide catalysts[1-6] and the other is concerned with the fate of organophosphorus compounds used as pesticides or nerve gases when they come into contact with soil.[6-13] In the latter context, there have been several studies of the adsorption of the nerve gas simulant dimethyl methylphosphonate (DMMP) on various metal oxides.[6-10]

In this study we have used ^{31}P magic angle spinning (MAS) NMR spectroscopy and infrared (IR) spectroscopy to examine the interaction of gaseous trimethyl phosphite [$P(OCH_3)_3$ or TMP] on silica, over a range of temperatures from 20 to 400 °C, with the aim of establishing the conditions which will lead to chemisorption or isomerization to dimethyl methylphosphonate, DMMP. Silica was chosen for this initial study because of the absence of Lewis acid/base sites so that coordination with the phosphorus lone pair electrons is avoided.[14] Therefore, chemisorption or isomerization is expected to arise solely from an interaction between TMP and the surface silanol (SiOH) groups. As will be discussed later, the combined NMR-IR approach provides a powerful probe of the resulting surface chemistry by virtue of the species selective (one signal per P atom) and quantitative (number of P atoms of each type) aspects of NMR,

and the qualitative (group frequency) and bonding specific (H bonding, physical or chemical adsorption) aspects of the infrared method.

Experimental Section

The silica used was Cab-O-Sil type HS-5 provided by the Cabot Corp. and had a BET (N_2) surface area of 325 m^2/g. For most experiments a standard pretreatment procedure involved vacuum activation for 1 h at 350 °C in the IR cell or in the NMR tube at a base pressure of about 10^{-5} Torr. When other conditions were used these will described in the text. For the IR experiments the powder was first pressed at about 10^7 Pa into self-supporting disks (25 mm diameter, 12.5 or 50 mg) prior to mounting in the IR cells for activation. For the NMR experiments 55-mg disks were broken up into small pieces and then placed in NMR tubes (see below).

Room temperature (23 ± 2 °C) IR experiments were carried out in a 300-mL quartz cell which has been described previously.[15] The high-temperature experiments were carried out in a quartz cylindrical cell 15 cm in length and 22 mm i.d. having a total volume of 78 mL. In the latter case the sample was placed in a slotted quartz holder in the center of the tube and the sample could be heated by an external furnace to the desired temperature. In these experiments the cell remained in a fixed position in the IR beam during the entire experiment. Infrared spectra were recorded on either a Bomem DA3-02 (MCT detector) or a Bomem Michelson MB100 (DTGS detector) Fourier transform spectrometer at a resolution of 2 cm^{-1}.

^{31}P NMR measurements were carried out on a 1.4 T instrument, giving a resonance frequency of 24.3 MHz for ^{31}P. Two types of excitation were used; for the study of weakly bound species, excitation was by 90-deg pulses, using the pulse sequence of Duncan et al.[16] to suppress artifacts. For more rigid species, single-contact Hartmann-Hahn cross polarization with spin temperature alternation was used.[17]

In both types of experiment a proton decoupling field of 55 kHz strength was used. This is sufficient to decouple direct bonded P-H dipolar interactions. In principle, 90-deg pulses give uniform excitation of all ^{31}P resonances. In practice, since spectra are signal averaged at a fixed time interval, resonances whose T_1 relaxation

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times are longer than this interval are attenuated. For most of the spectra in this work a repetition interval of 1 s was used. Cross polarization, on the other hand, specifically excites ^{31}P with a significant dipolar coupling to ^{1}H and hence is biased in favor of immobile species with short P–H distances. Signal enhancement by a factor of 2.5, and repeatability on the ^{1}H relaxation time scale, make cross polarization much more sensitive for the detection of small quantities of such species.

For the detection of direct P–H bonding, two methods were used. With mobile species, it was sufficient to turn off the decoupler and observe the large single-bond coupling. For rigid species, cross polarization with a 70-μs decoupler delay was used.[18] This completely eliminates signals from P–H bonded species, but only partially attenuates signals from ^{31}P with more distant ^{1}H.

Samples for NMR study were prepared on a vacuum line, in 5-mm NMR tubes, which were sealed after sample preparation. For samples involving high-temperature reaction with TMP, the NMR tube was sealed to a larger tube of 120-mL volume. Reaction occurred with the SiO_2 spread in a thin layer on the bottom of the latter and the SiO_2 was poured under vacuum into the NMR tube, which was then sealed. For studies involving time evolution of species, TMP was condensed into a liquid nitrogen cooled sample of silica. The time of reaction in these studies is taken as the interval between removal of the sample from the dewar and the midpoint of the corresponding NMR measurements. For these studies, the NMR data accumulation took 4.5 min. The sealed tubes were spun at the magic angle by using a spinner previously described.[19] Spinning rates between 2 and 3 kHz were used in the present investigation. NMR measurements were carried out at 23 ± 2 °C.
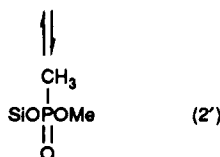
Trimethyl phosphite (TMP) was purchased from Aldrich and had a stated purity of >99%. The ^{31}P NMR spectrum of liquid TMP indicated that there was less than 0.1% P-containing species as impurities.

Results

(*a*) *Adsorption at 23 °C, NMR Spectra.* The aerosil silica used in this work has about 1.6 ± 0.1 accessible isolated SiOH groups/nm^2 after activation under vacuum at 350 °C (as measured gravimetrically from SiOH/SiOD exchange with ND_3) and a small number of "inaccessible" silanols which are perturbed due to interparticle contact.[14] Therefore, the number of accessible silanols is about 0.86 mmol/g of silica.

Ten minutes after warming a sample in which 1.58 mmol/g of TMP was condensed, the ^{31}P NMR spectrum showed a strong peak at 142 ppm and a weak one at 12 ppm (Figure 1A). The latter had a P–H coupling of 720 ± 20 Hz. Liquid TMP has a chemical shift of 140 ppm; dimethyl phosphite (DMP) has a shift of 11 ppm, and a P–H coupling of 700 Hz. Thus it is clear that the observed peaks are unreacted TMP, together with some DMP. Both resonances remain narrow in the absence of proton decoupling, and no spinning side bands are seen. Thus both species must be moving with considerable freedom on the surface.

TMP might be expected to react with SiOH through one of the following routes:

$$SiOH + P(OMe)_3 \longrightarrow SiOMe + O{=}P(OMe)_2 \qquad (1)$$

$$SiOH + P(OMe)_3 \longrightarrow CH_3OH + SiOP(OMe)_2 \qquad (2)$$

$$\Updownarrow$$

$$\underset{\underset{O}{\overset{\|}{\mathrm{SiOPOMe}}}}{\overset{\overset{CH_3}{|}}{}} \qquad (2')$$

The observed spectrum for short reaction times suggests that only (1) is occurring. Further evidence, to be presented below, shows that (1) is indeed the initial reaction, and there is no evidence for
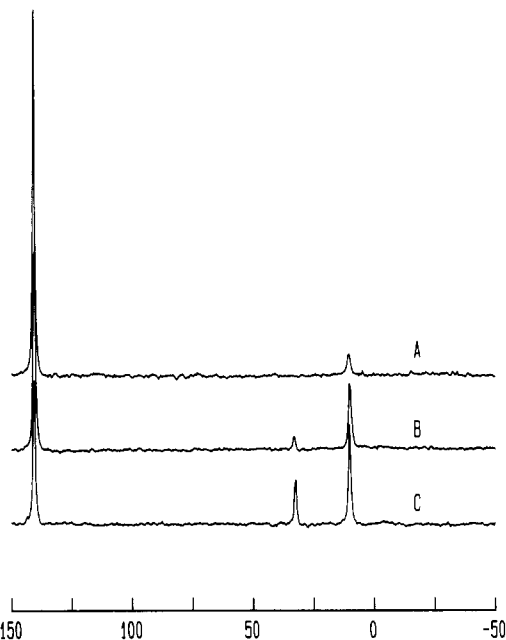
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Figure 1. Room temperature ^{31}P NMR spectra for 350 °C activated silica with 1.58 mmol of TMP per g of SiO_2: (A) 10 min after warming sample to room temperature; (B) after 235 min; (C) after 1360 min. The chemical shifts (*x* axis) are with respect to H_3PO_4.

products of (2) or (2′) at 23 °C, even after long reaction times.

During the next 50 min the TMP signal rapidly decreased while that due to DMP increased and, after a total reaction time of 60 min, a new weak signal was detected at 36 ppm. This signal slowly increased over the next 1500 min while the trend of the TMP and DMP signals continued as before. Figure 1, B and C, shows the spectra after 235 and 1360 min, respectively, and Figure 2A shows a plot of the integrated intensities of these three signals over 1500 min, and the sum of the integrated intensities of these three signals. The 36 ppm resonance is close to that for liquid DMMP at 32 ppm and, therefore, we assume that the isomerized form of TMP is also produced via (3) which is catalyzed by silica. As will be

$$P(OMe)_3 \rightleftharpoons (OMe)_2P({=}O)CH_3 \qquad (3)$$
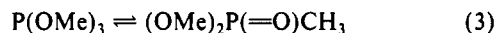
discussed further below, the products DMP and DMMP were also identified by infrared spectroscopy and mass spectrometry. Therefore, we conclude that at 23 °C the reaction between this silica and TMP primarily yields DMP via reaction 1 accompanied by a small quantity of DMMP via reaction 3. The near constancy of the total phosphorus signal in Figure 2A indicates that these are the only major reactions and the relatively constant value of the DMP signal after about 800 min indicates that reaction 1 had essentially ceased.

The quantity of DMMP produced after 1500 min reaction in plot 2A was 21 μmol. When a smaller quantity of TMP was added, 45 μmol (nearly equal to the number of SiOH groups) a curve similar to that shown in Figure 2A was observed (not shown) except that less DMMP was produced with time, being 5.7 μmol after 1500 min. With half this amount of TMP, 22 μmol, no DMMP was detected until 1200 min and 1.1 μmol was present after 1500 min. For both the 45 and 22 μmol TMP experiments, the tendency of DMP to reach a constant plateau was less evident, particularly with the smaller initial dose. Finally, the initial rates of formation of DMP also decreased with decreasing TMP dose, after 100 min reaction the quantities produced being 20, 12, and 6.5 μmol, respectively. These and other results for the three reaction conditions are summarized in Table I and will be discussed further later.

Two additional experiments were carried out in order to determine how the concentration of SiOH groups would influence the course of the reaction. Silicas were activated at 650 °C (1.0 ± 0.1 SiOH/nm^2) or 900 °C (0.5 ± 0.1 SiOH/nm^2), and the same quantity of TMP/g of silica was added to each as was used to obtain the data shown in Figure 2A. The results are plotted in
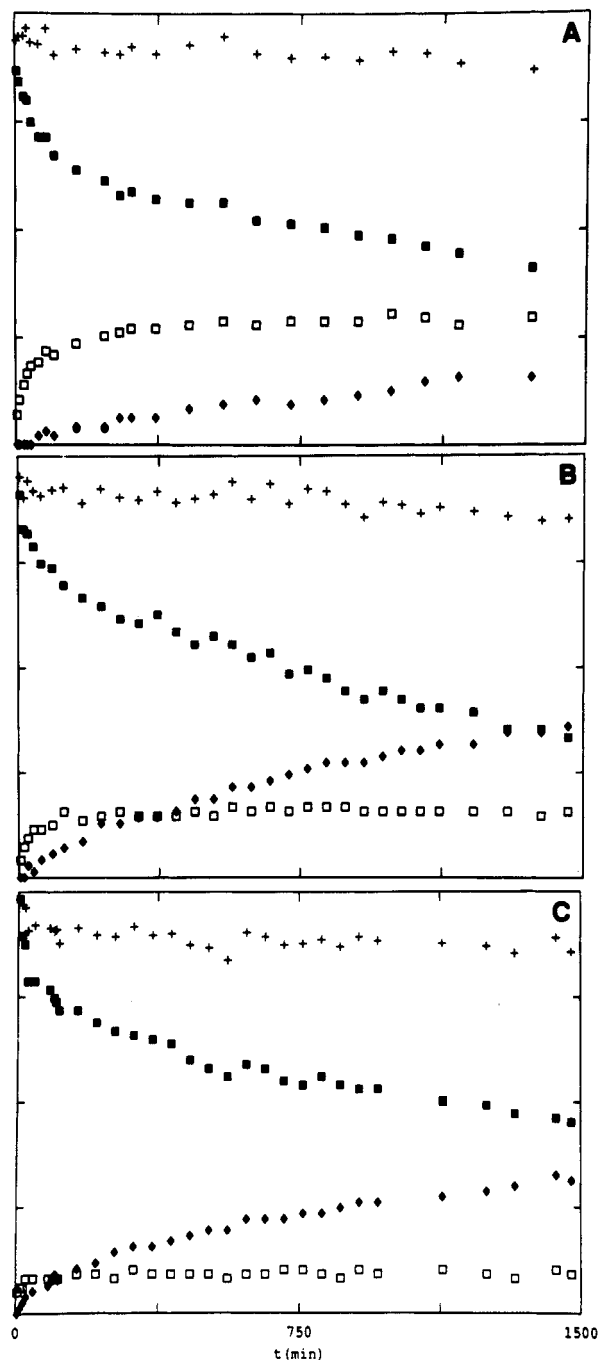
Figure 2. Time evolution of the integrated intensities of the ^{31}P signal of TMP (■), DMP (□), and DMMP (◆). The sum of the integrated areas of these three signals is +. In each case 1.58 mmol/g of TMP was used and the activation temperatures of the silica prior to admission of TMP were (A) 350 °C, (B) 650 °C, (C) 900 °C.

TABLE I: TMP Adsorption Data for 350 °C Activation

1. TMP added, mmol/g	1.58	0.82	0.40
2. TMP added,[a] μmol	87	45	22
3. ratio TMP/SiOH[b]	1.9	1.0	0.5
4. μmol TMP (1500 min)	37	17	3.9
5. μmol DMMP (1500 min)	21	5.7	1.1
6. μmol DMP (1500 min)	29	22	17
7. μmol DMP (100 min)	20	12	6.5

[a] For 55 mg of silica. [b] The SiO_2 contained 0.86 mmol/g SiOH = 47 μmol for 55 mg of sample.

Figure 2, B and C, for 650 and 900 °C activation, respectively. Qualitatively, less DMP and more DMMP is produced relative to that for curve 2A, and in both cases, the production of DMP reaches an almost constant plateau after a relatively short period into the reaction. The three curves (2A, 2B, and 2C) show that
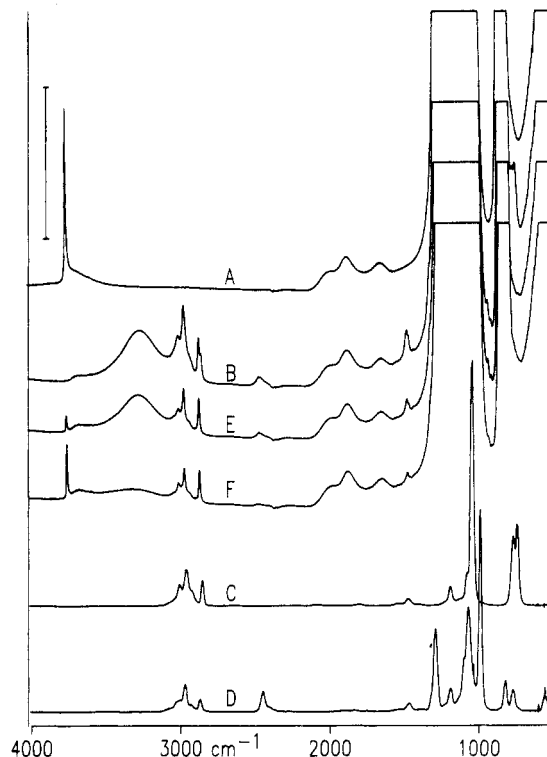
Figure 3. (A) Infrared spectrum of a 10 mg/cm² SiO_2 disk at 23 °C after vacuum activation at 350 °C; (B) 20 h after addition of 1.0 mmol/g of TMP; (C, D) infrared spectra of 2.0 Torr of gaseous TMP and DMP, respectively, in a 10-cm gas cell; (E, F) infrared spectra as for curve B after 5 min and 20 h evacuation, respectively. The bar at the top left represents an absorbance of 1.0 for A, B, E, and F, 0.75 for C, and 0.25 for D.

the DMMP/DMP ratio apparently increases with the temperature of activation of the silica.

(b) *Adsorption at 23 °C, Infrared Spectra.* The infrared spectrum of a 10 mg/cm² self-supporting silica disk after activation under vacuum for 1 h at 350 °C is shown in Figure 3A. The strong sharp peak at 3747 cm⁻¹ is due to isolated surface silanol groups and the broad features below 2000 cm⁻¹ are mainly due to overtone and fundamental modes[14] of bulk SiO_2. Such disks are opaque between about 1275–1000 and 850–750 cm⁻¹. If the quantity of silica is reduced to about 2.5 mg/cm², which is the lower limit for a self-supporting aerosil disk, the latter region exhibits limited transmission (peak maximum at 800 cm⁻¹, absorbance 1.0)[14] and only the spectral region from 1250 to 1010 cm⁻¹ is inaccessible. In some of the spectra to be shown below, the background spectrum of the activated silica has been subtracted from that observed after adsorption of TMP.

Twenty hours following the admission of about 1.0 mmol/g of TMP to the above sample the spectrum in Figure 3B was observed. The strong bands from 3000 to 2800 cm⁻¹ are mainly due to the CH_3 stretching modes of gas-phase TMP, the weak band near 2450 cm⁻¹ is the PH stretching mode of DMP, and very weak absorptions near 900 cm⁻¹ in the region of partial transmission are due to DMMP. The basis of these assignments and expanded spectra in the 2450- and 900-cm⁻¹ spectral regions will be discussed in more detail below. Figure 3, C and D, shows the spectra of gas-phase TMP and DMP, respectively. Using established group frequencies[20] and published data,[21-23] the vibrational assignments for TMP, DMP, and DMMP are listed in Table II.

Figure 4 shows details of the spectral changes in the 3800–2400-cm⁻¹ spectral region which occurred over a 20-h period (in this experiment, 2.0 mmol/g of TMP was added). The sharp 3747-cm⁻¹ band was immediately replaced by a broad band at

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TABLE II: Group Frequencies (cm⁻¹) for Various P–X Functional Groups[a]

vibration	POCH$_3$	PCH$_3$
(CH$_3$)	3005–2995 (w)	3005–2995 (w)
	2960–2950 (s)	2930–2920 (w)
	2860–2840 (s)	
(CH$_3$)	1475–1460 (m)	1425–1415 (vw)
	1250–1230 (w)	1325–1315 (m)
(CH$_3$)	1190–1170 (m)	920–890 (s)
O–C	1050–980 (vs)	
O–P	830–740 (s)	
P–C		730–680 (w)
	Miscellaneous	
P=O	1300–1240[b]	
	1240 (DMMP liquid)	
	1286 (DMP gas)	
	1265 (DMP liq)	
P–H	2443 (DMP gas)	
	2430 (DMP liq)	

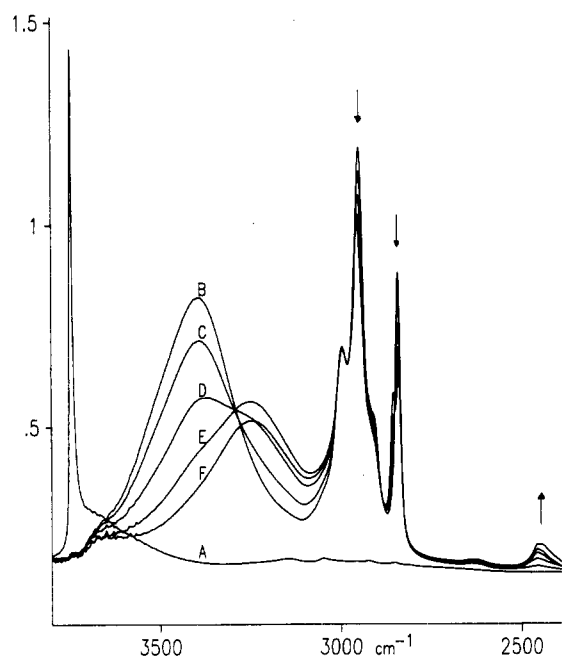[a] From refs 7, 10, and 20–23. [b] General range for noninteracting P=O.

Figure 4. Infrared spectra of a 10 mg/cm² SiO$_2$ at 23 °C after activation at 350 °C: (A) before addition of TMP; (B) 1 min after addition of 2.0 mmol/g of TMP. Subsequent spectra show the time evolution of the reaction after (C) 30 min, (D) 2 h, (E) 6 h, (F) 20 h.

3390 cm⁻¹ characteristic of a hydrogen-bonding interaction between SiOH and TMP. The 3390-cm⁻¹ band shifted with time to 3250 cm⁻¹, a shoulder grew to high wavenumber of the sharp 2840-cm⁻¹ peak, and a new weak asymmetric band appeared having a maximum at 2457 cm⁻¹ and a shoulder at 2440 cm⁻¹. A band in the 2400–2470-cm⁻¹ spectral region is indicative of the presence of PH-containing species[20,22] and Figure 5A shows the evolution of this band on an expanded wavenumber scale. An infrared and mass spectroscopic analysis of the species which could be trapped in a liquid nitrogen trap following evacuation after about 30 min reaction showed that TMP and DMP were present. Finally, adsorption of TMP on a fully deuterated silica similarly activated (SiOD = 2760 cm⁻¹) gave identical spectral features except that the 3400–3200-cm⁻¹ features shifted to 2300–2200 cm⁻¹ and the 2457-cm⁻¹ band appeared at 1792 cm⁻¹. The downward shift by a factor of 1.38 is expected for H/D stretching modes.[20,24]

For greater than about 1 h reaction, new weak bands appeared at 1421, 1315, 920, and 900 cm⁻¹ which steadily grew in intensity

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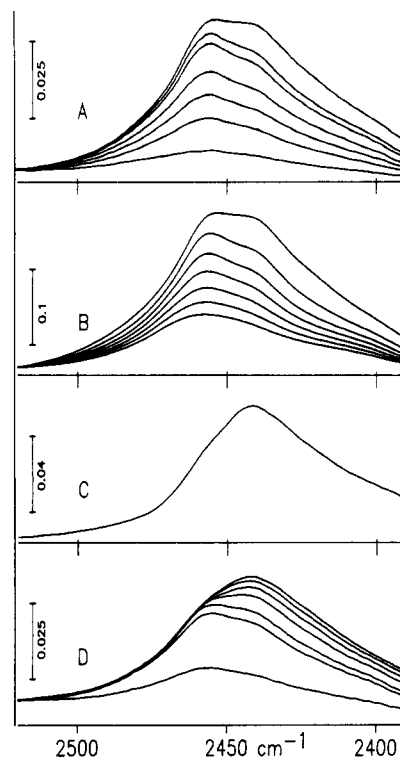

Figure 5. (A) Time evolution in the PH stretching spectral region for the experiment described in Figure 4. The band is growing in intensity and the spectra shown were recorded 1 min after addition of TMP and after 30 min, 1 h, 2 h, 4 h, 6 h, and 20 h reaction. (B) Adsorption at 23 °C of DMP (see text) on 350 °C activated SiO$_2$ (top curve) and evolution of the spectra (decreasing intensity) after evacuation for 1, 5, 15, 45, 105, and 240 min. (C) Infrared spectrum of DMP adsorbed on a methoxylated silica after conversion of the SiOH groups to SiOCH$_3$. (D) Adsorption at 23 °C of 1.7 mmol/g of TMP on a 1000 °C activated silica (bottom curve) and evolution of the spectra (increasing intensity) after 30 min, 1 h, 3 h, 7 h, 11 h, and 20 h reaction.
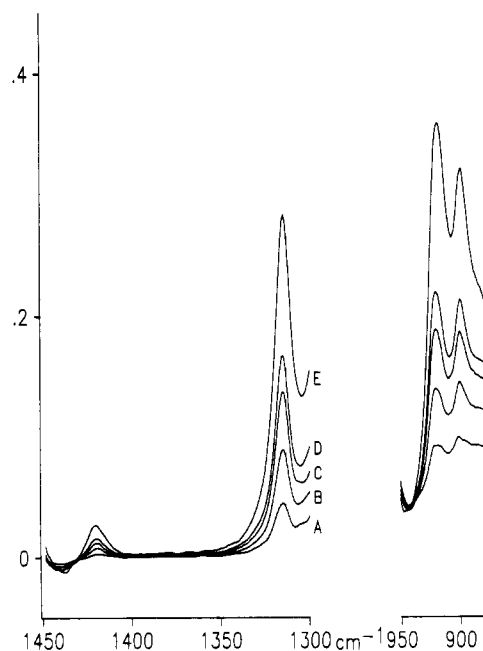

Figure 6. Difference spectra showing the growth of the DMMP bands on an 800 °C activated silica after addition of 1.6 mmol/g of TMP as 23 °C. The difference spectra were obtained by subtracting the spectrum observed immediately after addition of TMP from those obtained after (A) 20 min, (B) 1 h, (C) 2 h, (D) 3 h, (E) 20 h.

with time (spectra for a different sample are shown in Figure 6). Evacuation through a cooled trap showed that a third product was present, identified via IR and MS to be DMMP. Phosphorus compounds containing a PCH$_3$ functional group have unique

PCH₃ deformation and rocking modes at the above frequencies which are not found for POCH₃ functional groups (see Table II), further confirming the presence of DMMP.

Figure 3, E and F, shows the spectral changes upon evacuation after 20 h reaction. Evacuation for 5 min (Figure 3E) resulted in partial restoration of the 3747-cm⁻¹ peak and a reduction in the intensity of the CH₃ stretching and deformation bands (3000 and 1470 cm⁻¹). After 20 h evacuation the 3747-cm⁻¹ band had regained 35% of its initial intensity, although there was still some residual H-bonded SiOH, and the peaks in the 2450- and 900-cm⁻¹ spectral regions due to DMP and DMMP, respectively, had not completely disappeared, showing how tenaciously both species adsorb. Evacuation or mild heating so as to remove the last traces of DMP and DMMP left a spectrum from 3000 to 1300 cm⁻¹ which was essentially identical with that shown in Figure 3F, having bands at 3000, 2958, 2858, and 1470 cm⁻¹, characteristic of SiOCH₃ groups on silica.[24] This species was stable up to 400 °C evacuation, confirming that the only chemisorbed surface species was indeed SiOCH₃. Therefore, in accord with the NMR results, reaction 1 appears to be the only dissociative process occurring at 23 °C, accompanied by the slower isomerization reaction 3 to produce DMMP. Note also that, even after 20 h, not all of the SiOH groups react at 23 °C.

A silica activated at 350 °C contains some SiOH groups which are inaccessible to larger molecules whereas one activated at 800 °C presents a relatively symmetrical SiOH peak and no inaccessible hydroxyls.[14,25] The adsorption of TMP on a 800 °C activated SiO₂ showed similar features in the 3800–2400-cm⁻¹ spectral region as reported above, and both DMP and DMMP were produced. The quantity of DMP was, as judged by the intensity in the PH spectral region, about 0.60 of that generated for a 350 °C activated sample but the quantity of DMMP (1315-cm⁻¹ band) was about 2.2 times greater. Figure 6 shows the evolution of the 1315/1421- and 920/901-cm⁻¹ peaks due to DMMP as a function of time up to 20 h. Subsequent evacuation for 48 h restored the SiOH intensity to about 40% of its original value and only the spectrum of SiOCH₃ was observed. This result is comparable to that found using NMR with a 900 °C activated sample.

(c) *High-Temperature Reactions.* Following adsorption of TMP for 20 h at 23 °C on a 350 °C activated silica, it was subsequently heated to various temperatures between 100 and 400 °C and, after cooling to 23 °C, the infrared spectra were recorded. The spectral changes were somewhat complex, suggestive of the formation of various new PH, POCH₃, and PCH₃ species, the group frequencies of which all lie in relatively narrow frequency domains.[20] The ³¹P NMR spectra under the same reaction conditions for each of the three samples previously described showed that up to seven new resonances were detected having chemical shifts in the range −17 to +22 ppm, a range usually associated with the formation of phosphate and polyphosphate-like species.[26] It is not possible to identify the nature of these species nor is this fruitful given the complexity of the reacting system where any or all of TMP, DMP, and DMMP might further chemisorb on silica, or react with each other, or react with chemisorbed products.

Although TMP is a relatively volatile species at 23 °C having a vapor pressure of about 40 Torr, those of DMP and DMMP are about 2 Torr and it is difficult to ascertain whether even a prolonged evacuation removes all traces of physically adsorbed DMP or DMMP from the surface of silica. Therefore, we have studied the adsorption of TMP on silica at temperatures at or above 100 °C where facile desorption of DMP and DMMP was expected during evacuation. In the IR experiments to be described below, all spectra were recorded with the sample at 100 °C.

Infrared spectra in the 3800–2400-cm⁻¹ spectral region following the adsorption of 1.0 mmol/g of TMP on SiO₂ at 100 °C (after 350 °C activation) are shown in Figure 7. Although a broad band appeared initially at about 3390 cm⁻¹ along with the PH band
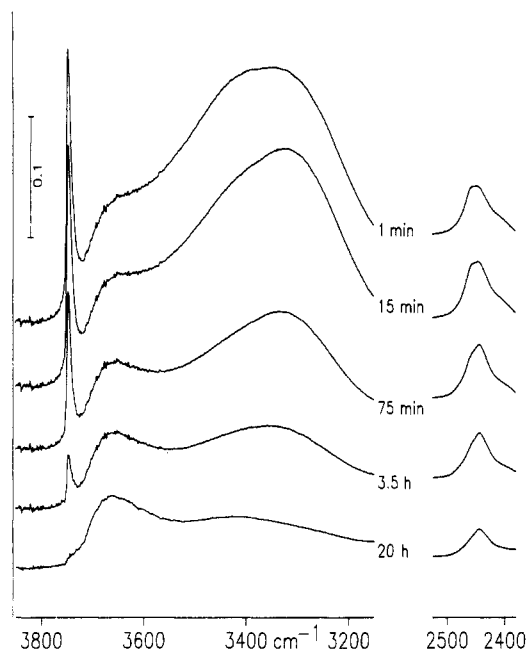

Figure 7. Infrared spectra observed following addition of 1.0 mmol/g of TMP to a 350 °C activated silica at 100 °C (all spectra recorded with the sample at 100 °C) after the indicated reaction times.

near 2450 cm⁻¹, the isolated SiOH peak did not immediately disappear but its intensity slowly decreased over about 4 h along with that of the 3390-cm⁻¹ band. (Figure 7 shows the residual 3747-cm⁻¹ intensity after 3.5 h; this peak was gone after 4 h.) Further, the PH band did not increase in intensity with time, but rather, the band shape changed as the 2457-cm⁻¹ peak decreased in intensity leaving that at 2440 cm⁻¹. Although the bottom spectrum shown in Figure 7 was for 20 h reaction, it was qualitatively similar to that observed after 4 h reaction except that the broad band at 3390 cm⁻¹ was slightly more intense after 4 h. Therefore, be it a 4-h or 20-h reaction most of the SiOH groups had essentially reacted. Brief evacuation of the gas phase after 20 h reaction removed all gas-phase species and left a weak residual peak at 2460 cm⁻¹. Analysis of the trapped evacuation products showed that only TMP and DMP were present and that, even after long reaction times, no DMMP was detected. These results show that reaction 1 goes to completion under these conditions and that isomerization to DMMP does not occur. The absence of DMMP at 100 °C was also verified in an NMR experiment.

Prolonged evacuation at 100 °C or even evacuation at 200 °C did not decrease the intensity of the 2460-cm⁻¹ peak discussed above, suggesting that a chemisorbed species was present. The boiling point of DMP is 175 °C and one would expect that evacuation under the above conditions would desorb all DMP. No other IR bands were detected by using a 10 mg/cm² disk and, because any P=O bands present would be hidden by bulk SiO₂ absorption between 1250 and 1300 cm⁻¹, we carried out an experiment with a 2.5 mg/cm² disk which is transparent to about 1250 cm⁻¹. After the 350 °C activation 2.4 mmol/g of TMP was allowed to react with the sample for 1 h at 100 °C. Figure 8 shows a series of difference spectra after subtraction of the silica background. Figure 8A was recorded with TMP present and peaks at 1465, 790, and 740 cm⁻¹ are due to adsorbed or gas-phase TMP. There are also weak bands at 2457 and 2440 cm⁻¹ (not shown) due to DMP; this species would also be expected (Table II, Figure 3D) to have modes at 1465 cm⁻¹ and in the 800–750-cm⁻¹ regions but these would be masked by those of the unreacted TMP which is in excess. In addition there is a peak at 1280 cm⁻¹ in the spectral region associated with unassociated P=O stretching vibrations (Table II) and a weak peak at 850 cm⁻¹ which is a known mode[27]

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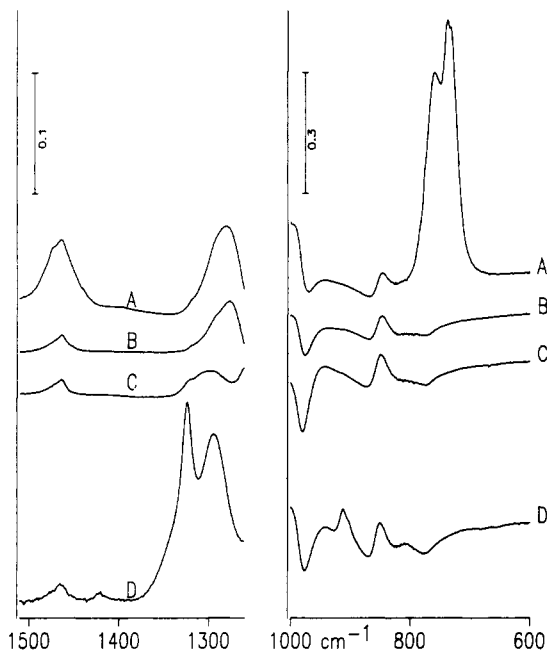
Figure 8. Difference infrared spectra observed the addition of 2.4 mmol/g of TMP to a 2.5 mg/cm^2 SiO$_2$ disk at 100 °C. The background spectrum of the 350 °C activated SiO$_2$ was subtracted in each case. (A) 1 h reaction; (B) evacuation of A for 15 min; (C) heating B under vacuum to 400 °C for 30 min and cooling to 100 °C; (D) readdition of 1.0 mmol/g of TMP to C at 100 °C, heating for 1 h to 350 °C, evacuation for 30 min at 350 °C, and cooling to 100 °C.

of SiOCH$_3$. Finally, the "negative" dip at 980 cm^{-1} is due to the disappearance of the SiO stretching mode[14] of surface SiOH groups which were converted to SiOCH$_3$ as the reaction proceeded.

Evacuation for 15 min (Figure 8B) removed the TMP (and DMP) leaving a band at 1280 cm^{-1} and weak bands at 850, 1470, (and 2460 cm^{-1}). Upon heating this sample at 400 °C under vacuum (Figure 8C) the intensity of the 1280-cm^{-1} peak decreased (there was a similar decrease in the intensity of the 2460-cm^{-1} band), its peak maximum shifted to 1295 cm^{-1} and a shoulder appeared at 1320 cm^{-1}. There were no further spectral changes with longer evacuation times.

This experiment shows that a strongly chemisorbed species is created during reaction at 100 °C which contains a PH mode and a P=O mode. The bands in the 800–740-cm^{-1} spectral region are associated with the O–P vibration of POCH$_3$ groups, and their absence after evacuation indicates that the surface species does not contain this functional group (these are normally strong bands, see Figure 3, C and D). The simplest structure which would account for these spectroscopic observations is a bridged species having the structure I:

The appearance of a very weak band near 1320 cm^{-1} suggestive of a PCH$_3$-containing species might indicate that a small number of species II is also present.

After the 1-h reaction above, only about 80% of the SiOH groups had reacted. A second 1.0 mmol/g dose of TMP was added to the sample at 100 °C, and the sample was heated to 350 °C for 1 h and then evacuated at 350 °C for 30 min. The spectrum in Figure 8D was observed, now having strong peaks at 1323 and 1295 cm^{-1}, accompanied by weaker bands at 1421, 913, and 902 cm^{-1}. These are the characteristic modes of a PCH$_3$ species. As a result of this last treatment, the PH mode at 2460 cm^{-1} disappeared, and we assume that species I was converted to species II.

In a different experiment, 0.40 mmol/g of TMP was added to a 10 mg/cm^2 sample at 25 °C (350 °C activation) and the temperature was raised to 400 °C, held there for 30 min, and then
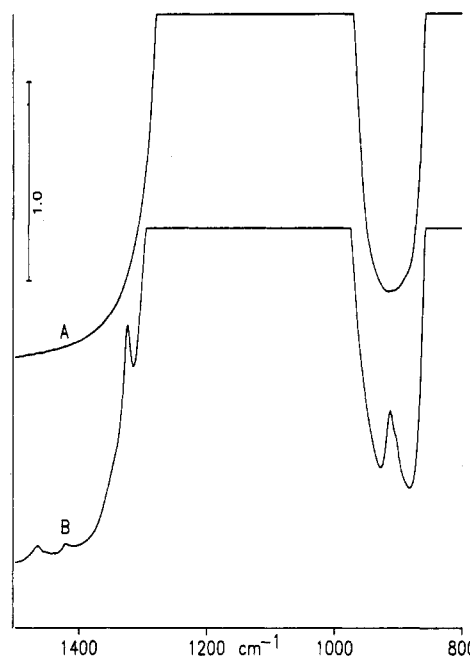
Figure 9. (A) Infrared spectrum of 10 mg/cm^2 SiO$_2$ at 23 °C after activation at 350 °C. (B) Infrared spectrum after addition of 0.4 mmol/g of TMP to A at 23 °C, raising temperature to 400 °C for 30 min, evacuation at 400 °C for 30 min, and cooling to 23 °C.
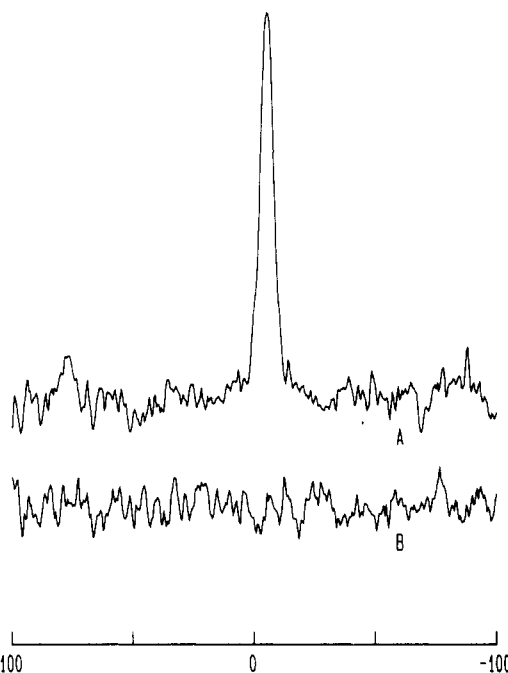
Figure 10. Room temperature ^{31}P NMR spectra recorded after reaction of 1.2 mmol/g of TMP for 1 h with SiO$_2$ at 100 °C (SiO$_2$ activated at 350 °C: (A) normal CP/MAS spectrum; (B) as for A but with 70 μs decoupler delay (see text). The chemical shifts (x axis) are with respect to H$_3$PO$_4$.

evacuated for 30 min. The IR spectra before and after reaction (1500–800 cm^{-1}) are shown in Figure 9. In addition to SiOCH$_3$ as a product, the new spectral features at 1421, 1323, 913, and 902 cm^{-1} are characteristic of a PCH$_3$-containing species, most probably structure II.

Therefore, the IR evidence suggests that a chemisorbed species having structure I is formed during reaction at 100 °C whereas, upon subsequently heating this in the presence of TMP to 350 °C, or by simply heating TMP/SiO$_2$ from 25 to 400 °C, structure II is favored.

NMR experiments were carried out in order to test whether the above hypotheses were plausible. A sample was activated at 350 °C and cooled to 100 °C, 1.2 mmol/g of TMP was added

curve (Figure no.)	2A	2B	2C
activation T, °C	350	650	900
(1) μmol DMP formed at plateau	27	16	8
(2) μmol TMP added	87	87	87
(3) μmol SiOH initially[a]	47	30	15
(4) μmol SiOH at plateau	20	14	7

[a] For 55 mg of SiO_2.

and allowed to react for 1 h, and then the sample was evacuated for 1 h at 100 °C. The ^{31}P spectrum (Figure 10A), observed by cross polarization, was found to consist of a single peak at −5 ppm. Delayed decoupling (Figure 10B) showed this to be an immobile species with a direct P–H bond. The long proton relaxation time, approximately 10 s, confirmed the absence of motion in this species. Observation of the spectrum at slow spinning speeds produced substantial spinning side bands and the chemical shift anisotropy was estimated, by the method of Herzfeld and Berger[28] as 172 ± 5 ppm. Both the shift and its anisotropy are consistent with a phosphite species such as I.

In a separate experiment 1.4 mmol/g of TMP was added to the 350 °C activated silica at about 40 °C; it was heated to 400 °C and held for 1 h, evacuated at 400 °C for 30 min, and cooled to 23 °C. A strong resonance at +9 ppm having a shoulder at +20 ppm was detected and neither species contained a PH bond. Further heating of this sample at 400 °C for an additional 90 min resulted in no change in the signal. The same spectra were also observed if TMP was added directly to a sample at 400 °C. These experiments are not inconsistent with structure II but additionally suggest that a second less predominant species might be present.

Discussion

(a) *Reaction Rates.* The results show that the major initial species produced from TMP adsorption on SiO_2 at 23 °C are physically adsorbed DMP and chemisorbed $SiOCH_3$. The isomerization of TMP to DMMP, although less favorable than reaction 1 initially at 23 °C, also occurs via (3).

The numbers in the first column of Table I for 1.58 mmol/g of TMP were mainly taken from the data that are plotted in Figure 2A. Plots for 0.82 and 0.40 mmol/g of TMP are not shown but data for these reactions are also given in Table I. The formation of DMP on all of the 350 °C activated samples occurs rapidly initially and qualitatively the initial rate is higher for a greater TMP/SiOH ratio (compare rows 3 and 7). The quantities of DMMP produced after long reaction times (1500 min, row 5) indicate a decrease in the extent of isomerization with decreasing dose of TMP. This is almost certainly related to the greater decrease in the amount of TMP when the TMP/SiOH ratio decreases. For example, after 1500 min, the quantity of TMP left unreacted (row 4) for the largest and smallest initial dose of TMP (37 vs 3.9 μmol, respectively) differs by a factor of 9.5, respectively, whereas the initial amounts (row 2) only differed by a factor of 4.0.

For the 350 °C (Figure 2A) sample, where the initial TMP concentration was greater than the SiOH concentration, one notes that after about 800 min the production of DMP has apparently reached a plateau in curve 2A. This plateau was reached much earlier for the 650 and 900 °C activated samples for the same initial dose of TMP (Figure 2, B and C). The very rapid initial rise in the DMP concentration followed by a plateau suggests that the production of DMP is rapidly inhibited shortly into the reaction. Some data pertaining to the reactions described in Figure 2A–C are given in Table III. Note that the quantities of DMP produced at the plateaux are approximately in the ratios of about 1:2:3.4 for 900, 650, and 350 °C activation, respectively. This ratio is nearly equal to the ratio of the initial number of SiOH groups present for these temperatures of activation (1:2:3.1). However, more important is the observation that the plateaus occur when the quantity of DMP formed is about *one half of the initial*

number of SiOH groups. Therefore, the reaction becomes strongly inhibited when half of the SiOH groups have reacted to yield DMP. A possible cause for this will be discussed below.

(b) *The Mechanism of the DMP Reaction.* The mechanism of the reaction to give DMP probably involves a variation of the Michaelis–Arbuzov rearrangement[29] as follows:

(4)
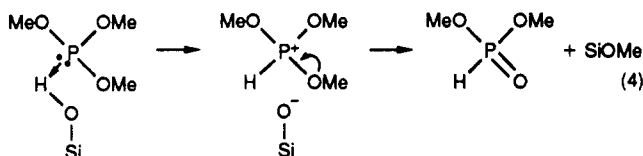
This mechanism explicitly involves an interaction of the lone pair electrons on phosphorus with the proton of an SiOH group. Although we cannot be specific as to the exact nature of the transition state, we know that the reaction apparently ceases when about half of the SiOH groups have been consumed. As will be discussed further below, DMP strongly H bonds with unreacted SiOH groups. Therefore, if DMP can migrate to an adjacent unreacted SiOH then, after 50% of the SiOH groups will have reacted, the remaining 50% will be H bonded to DMP and we assume that these sites do not permit formation of the necessary transition state for reaction 4 to occur. This might explain why the reaction effectively ceases when half of the SiOH groups are consumed. As will be discussed below, this does not prevent the isomerization to DMMP.

(c) *The Mechanism of the DMMP Reaction.* The isomerization reaction at 23 °C with a 350 °C activated silica is a minor side reaction but is relatively more important for a silica activated at 650–1000 °C. The IR and NMR data have shown that more DMMP relative to DMP is produced when (a) the silica has been activated at higher temperatures, and (b) when TMP is in excess relative to the number of silanol groups for activation at 350 °C. This suggests that there may be sites on silica which play a catalytic role in the isomerization process.

A silica which has been activated at temperatures above 450 °C has reactive sites (characterized by IR bands at 908 and 888 cm^{-1}) which exhibit Lewis acidity[30] and we considered that the greater extent of production of DMMP relative to DMP on the high temperature activated samples might be due to the presence of these sites. To test this, a silica was activated at about 1000 °C and sufficient methanol was added so as to just consume these sites.[30] TMP was added and, as with the previous 650–900 °C activated samples, a similarly large quantity of DMMP relative to DMP was produced. Therefore, we conclude that the Lewis sites created as a result of the activation are not responsible for the isomerization.

The reaction leading to DMP consumes SiOH and generates $SiOCH_3$ according to (4). Therefore, on a surface that has undergone partial reaction with TMP, both SiOH and $SiOCH_3$ are present and it is conceivable that either of these could catalyze the isomerization of TMP to DMMP.

In order to test whether $SiOCH_3$ alone are implicated in the isomerization reaction, we studied the reactivity of TMP on a highly methoxylated silica which had been activated at 350 °C and subsequently methoxylated at 400 °C with CH_3OH such that about 95% of SiOH was converted to $SiOCH_3$ (it is very difficult to achieve greater than about 95% conversion via this method). After addition of TMP, DMMP was again formed after 24 h, in quantities that were about 50–75% of that formed on a non-methoxylated silica.

The above was an ambiguous result which led us initially to suspect that $SiOCH_3$ generated via (4) was responsible for the catalyzed isomerization to DMMP. That is, with CH_3 replacing H in (4) one might have a catalyzed process which gives DMMP as the product. However, in a similar experiment using a 350 °C activated sample which was methoxylated with CD_3OD to give about 95% $SiOCD_3$ the same quantity of PCH_3-containing DMMP was produced as in the experiment with non-deuterated

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methanol. Therefore, although reaction 4 probably describes the mechanism of formation of DMP, it cannot (with H replaced by CH_3) describe the mechanism of isomerization of TMP to DMMP.

As a second approach to producing a methoxylated surface which contained no SiOH, a silica was activated at 1000 °C so that all inaccessible silanols would be removed and the sample was methoxylated at 400 °C via repeated exchange with MeOH over a 24-h period. Because water is a product of the methoxylation a very small number of H-bonded silanols re-formed, as evidenced by the appearance of an extremely weak broad band at about 3600 cm⁻¹. These silanols were then reacted with hexamethyldisilazane, HMDS, resulting in their conversion to SiOSiMe₃. We estimate from infrared intensities of the resultant SiOMe and SiOSiMe₃ species that the silanols created after activation at 1000 °C were >95% replaced by the former and the rest by the latter. Finally, following addition of 1.5 mmol/g of TMP to this sample for 24 h, no DMMP (or other product) was detected.

The above indicates that silanol groups rather than methoxyl groups are implicated in the isomerization. A plausible mechanism involving a SiOH group as a catalyst would involve the transfer of the proton on SiOH to the oxygen of a methoxyl group rather than to the P atom as in (4), as follows:
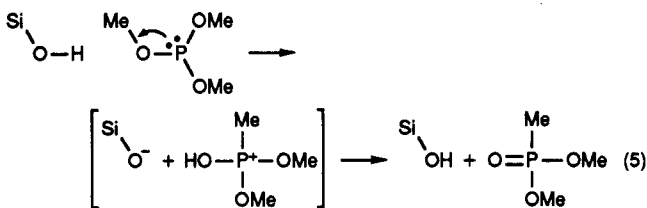
As long as SiOH groups remain accessible to the reactant, however many are present, isomerization would be possible. Note that the restrictions on forming the necessary transition state in (5) might be less severe than for reaction 4 because of there being three equivalent methoxyl groups in TMP which are more distant from the central P atom. Therefore, even in the presence of an adsorbed layer of DMP, isomerization may still be a facile process.

(*d*) *The PH Band at 2460–40 cm⁻¹ and the Role of Hydrogen Bonding.* Figure 5A shows the evolution of the PH band of DMP during reaction on a 350 °C activated sample. In Figure 5B we show spectra of DMP alone adsorbed on a similarly activated silica, as a function of the time of evacuation. The most intense spectrum was observed following adsorption of sufficient DMP such that the isolated SiOH peak at 3747 cm⁻¹ had disappeared giving rise to an intense broad band at 3200 cm⁻¹ due to H bonding with DMP (we have verified that DMP does not chemisorb on silica). The subsequent spectra were recorded following evacuation at the indicated times and the intensity variation and changes in band shape as DMP desorbed were very similar to those shown in Figure 5A for the TMP reaction itself. One notes that the low-wavenumber component at 2440 cm⁻¹ disappeared first following evacuation. In a separate experiment DMP was added to a silica in which all hydroxyl groups had been reacted with TMP. The PH peak which was observed is shown Figure 5C and has its peak maximum at the lower wavenumber with no apparent shoulder at 2460 cm⁻¹. Gaseous DMP has a symmetrical PH peak at 2443 cm⁻¹ and in liquid DMP it is at 2435 cm⁻¹. Therefore, we conclude that the 2460-cm⁻¹ peak is due to DMP which is H bonded to SiOH and that the 2440-cm⁻¹ peak is due to physically adsorbed DMP.

Figure 5D shows the time evolution of the spectra in the PH spectral region during the reaction of TMP on the 1000 °C activated sample discussed above. Note that after about 1 h reaction the formation of DMP clearly slowed down and virtually ceased after 3 h or 180 min (this is consistent with the previous IR and NMR results for 800 and 900 °C activation). The integrated intensity of this band after 3 h was 87% of that after 20 h reaction, clearly showing that there was a sort of "plateau" in the production of DMP. Beyond 3 h reaction, difference spectra (not shown) revealed that all of the "new" intensity was at 2440 cm⁻¹. Therefore, the additional DMP after about 3 h ended up being

physically adsorbed on the surface, even though silanol groups were still available. [The 87% figure for relative band areas quoted above is not to be considered a meaningful quantitative result for the proportions of H-bonded and physisorbed DMP, nor for the fraction of total DMP produced after 3 vs 20 h reaction, because we do not know the integrated absorption coefficients of these two species.]

The infrared results discussed above clearly support the ideas gleaned from the NMR data, but also show that H-bonding and diffusional effects can influence the course of this complex reaction. We will discuss this in the next section.

(*e*) *Steric and Diffusional Effects.* To complete the discussion of the room temperature reaction we want to account for the observation that the SiOH-catalyzed isomerization of TMP yields a greater quantity of DMMP on the more highly activated silicas where the numbers of SiOH groups are lower initially. Until the plateau is reached, DMP and SiOCH₃ are forming as SiOH is consumed. Beyond the plateau, the quantities of DMP, SiOH, and SiOCH₃ are almost constant. Most of the DMP is generated after the plateaus are reached, particularly for the 650 and 900 °C activated samples and, although not shown in Figure 2, DMMP growth continued for at least 100 h. Therefore, during this regime, isomerization is the major process occurring.

The data given in row 1 of Table III show that the major difference between the three samples studied is that there is more DMP at the plateau for a lower activation temperature. It follows that there is also proportionally less "free space" on these samples. That is, for the highest number of silanols initially, a greater proportion of the surface is occupied by DMP and SiOCH₃ at the plateau. It is not possible to determine whether it is the reduction in this free space or the greater amount of DMP that inhibits the rate of formation of DMMP. However, given that isomerization is still a relatively facile process on a methoxylated surface which contains a small number of SiOH and almost no DMP, we suggest that the greater quantity of DMP produced on the more highly hydroxylated silica is probably the major contributing factor. More DMP combined with less free space probably severely inhibits diffusion of reactants and products on the surface, making it more difficult to achieve the necessary transition state for isomerization. Further speculation is unwarranted.

(*f*) *Reactions at Higher Temperatures.* The reaction between TMP and silica at 100 °C generated DMP rapidly and the reaction went to completion in about 4 h. That the intensity in the PH spectral region (Figure 7) did not increase with time after the initial introduction of TMP is presumably related to the desorption of H-bonded DMP as SiOH was consumed. During the course of the reaction the H-bonded peak at 2457 cm⁻¹ decreased whereas that due to physically adsorbed DMP at 2440 cm⁻¹ remained relatively constant up to 3.5 h reaction and then decreased for 20 h reaction (Figure 7). This evolution is consistent with the SiOH spectral region which also shows, by virtue of the decrease in intensity of the isolated and H-bonded silanol bands, that SiOH is consumed relatively rapidly at this temperature.

As opposed to the reaction at 23 °C, a phosphorus-containing chemisorbed species was produced and, most strikingly, no DMMP was generated. The latter result was unexpected and will be discussed first. Recall that this reaction was only studied for a 350 °C activated silica.

The vapor pressures of TMP and DMP (and DMMP) are considerable at 100 °C and we assume that physical adsorption would be less favorable than at 23 °C. The chemisorption reaction which yields DMP is favored initially over isomerization even at 23 °C and this appears to be very much more the case at 100 °C. Therefore, either the silanols are consumed too rapidly to permit significant isomerization or the residence time which is required to give rise to the necessary transition state for the isomerization of TMP is not possible at 100 °C. Because we cannot measure the activation energies and preexpential factors of either reaction at 23 °C, further comment is not warranted.

The nature of the chemisorbed species formed at 100 or 400 °C needs little additional discussion. Species I is a relatively minor

chemisorbed product during reaction at 100 °C and this is relatively stable up to 400 °C evacuation. Species II containing a PCH_3 functional group is created when the reaction with TMP is carried out at 400 °C, or if excess TMP is added at a lower temperature and the sample is subsequently heated to 400 °C.

The nature of the reaction at 400 °C is obscure because we have found that, if TMP is heated to about 350 °C in the absence of silica, some isomerization occurs in the quartz IR cell whereas none occurs below 325 °C. Therefore, it is difficult to say whether II forms from TMP and silica or from DMMP and silica. Templeton and Weinberg[7] suggested that the reaction of DMMP with Al_2O_3 at 400 °C gave a species $(AlO)_3PCH_3$. In spite of having a four-coordinated P atom, the IEETS spectrum indicated that a P=O bond was absent. Species II definitely has a P=O bond and the assignment is justified based on the limited data available.

Conclusions

The major conclusions of this work can be summarized as follows:

1. At 23 °C TMP reacts rapidly initially with SiOH groups on silica to give chemisorbed $SiOCH_3$ and H-bonded DMP. The product DMP inhibits further reaction which virtually ceases after about half of the SiOH has been consumed. The inhibition arises because of the very strong H-bonded interaction between DMP and the unreacted SiOH groups.

2. SiOH catalyzes the isomerization of TMP to DMMP at 23 °C and the quantity of DMMP produced increases as the number of SiOH groups decreases. This is related to the decrease in the amount of DMP produced and the blocking effect of DMP on the isomerization. DMMP is also strongly H bonded to residual SiOH groups.

3. A mechanism for the formation of DMP and DMMP has been suggested and the role of diffusion and steric inhibition has been discussed.

4. At 100 °C the reaction of TMP to give DMP is so strongly favored that all accessible SiOH groups are consumed and isom-

erization of TMP to DMMP does not occur. In addition to DMP, a small quantity of a chemisorbed species having the proposed structure **1** is produced. This species is stable up to 400 °C.

5. When TMP/SiO_2 is heated from 23 to 400 °C, in addition to $SiOCH_3$ a new strongly chemisorbed species arises having the proposed structure **2**, plus a smaller quantity of an as yet unidentified species. The nature of this reaction is obscure because
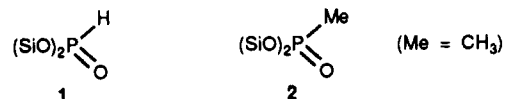
TMP itself isomerizes in the gas phase to DMMP even in the absence of silica at about 350 °C.

Finally, this study illustrates the power of a combined IR/NMR approach for studying a problem of this nature. The details provided above could not have been deduced by using either technique alone. We summarize these advantages as follows:

NMR. NMR spectroscopy clearly showed which species were mobile or immobile [physically and H-bonded species as opposed to chemisorbed species] and provided essential quantitative data relative to the proportions of various P-containing species during reaction at 23 °C. Such information is difficult to obtain by using IR alone.

IR. IR showed details of the fine structure of the adsorption and chemisorption processes, e.g., H bonding, changes in H bonding during reaction, and the distinction between H-bonded and physically adsorbed DMP, and it quickly demonstrated that $SiOCH_3$ was not a catalyst in the isomerization of TMP to DMMP. IR also showed that a chemisorbed species which contained a single $POCH_3$ group could not have been created after reaction at 100 or 400 °C.

Application of HREELS to Model Catalysts: CO and C₂H₄ Adsorption on Pt/Al₂O₃

D. A. Hensley and L. L. Kesmodel*

Department of Physics and Materials Research Institute, Indiana University, Bloomington, Indiana 47405
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A model catalyst made by Pt vapor deposition onto a thin alumina film is investigated with TEM and HREELS. The preparation techniques are fully described, and then the results of TEM analysis for Pt deposits in the range $(0.2-5.3) \times 10^{15}$ atoms/cm² are reported, for which clusters varying from 1.0 to 1.6 nm in diameter are observed. HREELS spectra are reported for the cases of CO and C_2H_4 adsorption onto the model. For the case of CO adsorption, it is shown that the catalyst is stable when heated to 500 K. For the case of ethylene adsorption, π and di-σ species are identified for adsorption at 165 K, but on warming to 325 K, ethylidyne is observed only for the larger Pt deposits. This is the first HREELS observation of the ethylidyne species on alumina-supported catalysts.

Introduction

The application of surface science spectroscopies to supported metal clusters as an attempt to model real catalyst systems has been a topic of much interest recently. Various techniques to model catalysts and characterize them with AES, XPS, HREELS, TEM, STM, and other surface science spectroscopies have been developed.[1-8] For vibrational spectroscopy, a goal has been to

use the wealth of information that has been gathered on single crystal–adsorbate systems as a base with which to interpret adsorption and reactions on transition-metal clusters.[1,9,10] In our previous work we have examined C_2H_4 adsorption on Pt vapor deposited onto TiO_2 and oxidized Al substrates.[11] The current work is a more complete examination of vapor-deposited Pt

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